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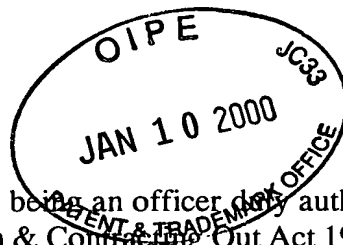
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30 APR 1997

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The Gillette Company
Prudential Tower Building
Boston
Massachusetts 02199
USA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

USA (Delaware)

4. Title of the invention

METHODS OF ELECTROFORMING COMPLEX THREE-DIMENSIONAL SHAPES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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**Methods of Electroforming Complex
Three-Dimensional Shapes**

5

This invention relates to methods of electroforming and to articles, e.g. shaving foils and pen barrels, made by the methods. The invention is applicable to methods of electroforming three-dimensional shapes which may be complex
10 shapes, e.g. shapes having a surface region where all points have non-zero Gaussian curvature.

As described in "VNR Concise Encyclopaedia of Mathematics" 2nd Edition (ISBN 0-442-20590-2) at pages 568 and 569, if the
15 Gaussian curvature of a curved surface at a point P has the value $k(P)$, three cases may be distinguished:

1. $k(P) > 0$, when the point P is called elliptic;
2. $k(P) < 0$, when the point P is called hyperbolic; and
- 20 3. $k(P) = 0$, when the point P is called parabolic.

This formal division has a close connection with the shape of the surface. For example, on a torus, the points towards the inside are hyperbolic and the points towards the outside are
25 elliptic. These two sets of points are separated from one another by two circles which consist of parabolic points. An ellipsoid has only elliptic points, a saddle surface has only hyperbolic points and a circular cylinder has only parabolic points.

30

In the past, shaving foils have usually been made in a flat condition. However, Japanese Patent Application No. 5-143093 (Publication No. 7-646) describes a method of manufacturing foils for electric shavers by electroforming a nickel layer
35 over a base member whose surface contains elliptic points.

The base member is formed by applying resist to a flat sheet of metal, patterning the resist and then deforming the metal sheet by a drawing process to form an elliptic surface. The method is limited by the fact that excessive deformation of the initially flat sheet could cause cracking of the resist layer.

The present applicant's own application WO93/19887 describes methods of manufacturing perforated foils for shavers in which a thin metal foil, supported on a flexible electrically insulating substrate, is patterned and subsequently thickened by electro deposition or electroless methods. One method described for patterning the metal film involves coating the film with an electrophoretic photoresist before exposing and developing the photoresist using a photographic artwork of the pattern of an electric shaver foil. The metal exposed after development of the photoresist is stripped in a solution of sulphuric acid and hydrogen peroxide. The remaining photoresist is then stripped to leave the flexible insulating substrate carrying the metal pattern. The document contains no suggestion of applying this technique to the electroforming of complex three-dimensional shapes.

An object of the invention is to provide a method of electroforming which can be readily applied to the electroforming of complex three-dimensional shapes, e.g. those having surfaces with non-zero Gaussian curvature.

According to one aspect of the invention, there is provided a method of electroforming in which:

(a) a layer of electrophoretic photoresist is applied to an electrically conductive mandrel by passing an electrical current therethrough;

- (b) the photoresist is exposed to a suitable source of electromagnetic radiation through a mask whose shape conforms closely to that of the mandrel;
- (c) the photoresist is developed; and
- 5 (d) a metallic layer is electrodeposited onto the exposed portions of the mandrel in the presence of the photoresist.

Since the photoresist is applied by electrodeposition, a reliable coating of resist may be achieved even if the
10 mandrel has a complex shape having non-zero Gaussian curvature.

Another object of the invention is to provide a method of manufacturing a three-dimensional mask for use in the
15 electroforming method.

According to another aspect of the invention, there is provided a method of manufacturing a three-dimensional electroforming mask for use in the method of electroforming
20 of said one aspect, comprising the following steps:

- (a) applying a photoresist to a flat surface;
- (b) patterning the photoresist by exposure and development steps;
- (c) electrodepositing a mask preform onto the flat surface;
- 25 and
- (d) pressing the preform into the desired three-dimensional shape.

30 According to a further aspect of the invention, there is provided a method of manufacturing a three-dimensional electroforming mask for use in the method of said one aspect of the invention comprising the following steps:

- a) apply a metallic coating to a substrate; and
- 35 b) pattern the coating by etching using a laser.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be
5 made by way of example to the accompanying drawings in which:

Fig. 1 is a schematic diagram of an assembly of mandrel, mask and cap;

Fig. 2 shows apparatus for coating the mandrel with
10 photoresist;

Fig. 3 shows schematically apparatus for exposing photoresist through the mask;

Fig. 4 shows apparatus for developing the photoresist;

15 Fig. 5 is a schematic diagram of apparatus for electrodepositing a metallic layer onto exposed portions of the mandrel;

Fig. 6 is a cross-sectional view on a diameter through a nickel electroform;

20 Fig. 7 shows a first pressing operation in the production of a mask;

Fig. 8 shows a mask preform after the first pressing operation;

Fig. 9 shows schematically a second pressing
25 operation in the formation of the mask;

Fig. 10 shows the mask after the second pressing operation;

Fig. 11 shows an isometric view of an electroplated plastic mandrel for making a pen barrel;

30 Fig. 12 shows schematically a milling operation performed on the mandrel of Fig. 11;

Fig. 13 shows an isometric view of a tubular metallic mask provided with shaped apertures;

Fig. 14 shows an isometric view of a generally conical
35 plastic mandrel having an electroplated surface;

Fig. 15 shows schematically a laser etching operation performed on the mandrel of Fig. 14;

Fig. 16 shows a generally conical metallic mask with etched patterning;

5 Fig. 17 shows an isometric view of a conical plastic mandrel provided with a flash silver coating;

Fig. 18 shows a tampo printing operation performed on the mandrel of Fig. 17;

10 Fig. 19 shows an isometric view of an electroplated mandrel;

Fig. 20 shows formation of a foil with an undercut;

Fig. 21 shows separation of the foil of Fig. 20 from the substrate; and

Fig. 22 shows another method of making a mask.

15

It has previously been difficult to electroform complicated surfaces having non-zero Gaussian curvature, although attempts have been made to use photolithography to expose a photoresist through a photo imaging mask. However, 20 conventional photoresists are usually applied as a liquid and therefore provide no control over the localised continuity of the photoresist. Whilst this may be satisfactory on a two-dimensional, flat surface, it causes difficulties if the photoresist is applied to a complex three-dimensional shape. 25 Current dry film photoresist is not suited to application onto complex shaped surfaces.

The present invention enables this problem to be addressed by the use of an electrophoretic photoresist. Such a resist can 30 be applied to a mandrel by the application of electric current. This not only causes the photoresist to adhere firmly to the substrate, but also produces a uniform thickness. Since the photoresist is non-conductive, the thickness is self-limiting. Thus, when the required thickness 35 is achieved, the passage of electric current ceases and the

deposition process is arrested. The thickness may nevertheless be controlled by adjustment of solution temperature, current density, voltage and deposition time. Such photoresists thus have the advantage of coating the
5 whole mandrel with a film of uniform thickness irrespective of the shape of the mandrel.

Electrophoretic photoresists can be applied to substrates by the passage of electric current between two electrodes
10 immersed in the photoresist solution. One of the electrodes is the substrate to be coated and this may be either anodic or cathodic. The thickness and continuity of the photoresist film are affected by the length of time the voltage is applied. If it is too long, the film will become porous
15 because of the evolution of gas bubbles, but if the time is too short the film will not be fully formed and will therefore again be porous. However, if the photoresist is correctly deposited it offers a pore-free coating of uniform thickness with improved adhesion over conventional
20 photoresists.

Referring now to the drawings in more detail, Fig. 1 shows a three-dimensional mandrel 1 supported by an electrical conductor rod 2, a mask 3, a transparent cap 4 and a plug
25 member 5.

The three-dimensional mandrel 1 is precisely machined from stainless steel to a required shape, which may be a complex shape curving in 2 or 3 dimensions. The surfaces onto which
30 an electroform is to be deposited are polished to remove any surface blemishes. Brass or another suitable material could alternatively be used for the mandrel. It may be made of plastics material provided with an electrically conductive surface coating, e.g. a thin silver coating.

The mask 3 may be manufactured from copper or any other suitable pliable metal, e.g. silver, by conventional two-dimensional electroforming as will be described hereinafter. Alternatively, the mask may be made by vacuum-forming a polyester layer over a suitable mandrel, as described hereinafter. The cap 4, preferably of perspex, has an internal cavity precisely matching the shape of the mandrel 1 for receiving the mask during the exposure step which will be described hereinafter. The mandrel 1, the mask 3 and the cap 4 all have a central aperture which is filled by the plug member 5 when the components are assembled together.

One process of manufacturing a nickel electroform will now be described with reference to Figures 2 to 5.

15

Both anodic and cathodic electrophoretic photoresists are available. Here, it is preferred to coat the shaped surface of the mandrel 1 cathodically with an electrophoretic photoresist, e.g. PCR3000TM manufactured by LVH Coatings Ltd. of Coleshill, Birmingham, U.K. To ensure good adhesion of the photoresist to the mandrel, suitable pre-treatment steps are used, using, for example, acid cleaner and rinsing agent.

The photoresist is then applied using the apparatus of Fig. 2. The mandrel 1, connected as cathode, and two anodes 21 are immersed in the electrophoretic photoresist 22 in a tank 23, which is held in a water bath 24.

It will be appreciated that storage of the photoresist and all operations following application of the photoresist to the substrate must be performed in subdued lighting, because the photoresist is light-sensitive. The coated mandrel is then thoroughly rinsed with rinsing agent and dried.

After the photoresist has been dried and allowed to cool, the preformed copper or polyester mask 3, retained in the cap 4, is then placed over the mandrel 1 as shown in Fig. 3. The assembly is processed by exposure to suitable radiation, e.g. ultraviolet light from source 31 in a light box 32 for sufficient time for the photoresist to be fully exposed. It may be required that the mandrel is inverted and re-exposed if the light box and mandrel designs do not allow the whole desired area to be exposed to radiation at the same time.

10

After the exposure steps, the mask and cap are removed from the mandrel. The photoresist is then developed as shown in Fig. 4 to produce a detailed negative photoresist image of the mask on the three-dimensional mandrel. After development, the mandrel is again rinsed and then cured at an elevated temperature.

Following developing of the photoresist all subsequent operations can be carried out in normal lighting.

20

The mandrel with its developed layer of photoresist must be pre-treated, prior to electroforming, to ensure that the subsequently deposited nickel layer is sound and to ensure that the nickel both fully conforms to the pattern imparted by the photoresist and yet can readily be parted from the mandrel. Ease of release can be effected by a surface passivation treatment e.g. using dichromate or other oxidising agent, dip or electrolytic pre-treatment.

30 Following the pre-treatment the metal layer is electroformed onto the mandrel using a suitable electrolyte 51 as shown in Fig. 5.

Fig. 5 shows the mandrel 1 as cathode on conductor rod 2, an anode 52, a heater 53 and a stirrer 54 all held in the electrolyte 51 contained in a tank 55.

5 Many electric razor foils currently produced have undercuts to reduce the friction between the underside of the foil and the cutter blades. Each undercut is an "indent" in the under side of the foil as shown in Fig. 20, where a foil 161 has an indent 162.

10

There are numerous methods of forming an undercut in a main foil 161:

a) Two-Dimensional Foils.

15

Undercuts on two-dimensional foils may be prepared as shown in Fig. 20 by electrodepositing a "pre-foil" 163 on a substrate 164 having a layer of photoresist 165. The "pre-foil" 163 is made of a suitable metal such as nickel, and is usually about 24 μm thick. The "pre-foil" 163 is passivated in 200 g/l sodium metabisulphite for 6-10 minutes at room temperature, after which the main foil 161 is deposited on top of the "pre-foil". Once the required thickness of the main foil has been achieved, the metal deposit is stripped from the substrate and the two foils are separated along the passivation layer, as shown in Fig.21.

20

25

b) Pre-Formed Foils.

30

Undercuts on pre-formed foils are created in the same manner as two-dimensional foils (as in a)), but difficulty can be experienced in separating the two foils if the pre-form shape is tightly curved.

c) Permanent Undercut.

35

An undercut can be formed in a foil by using a "permanent undercut" whereby a mandrel is preshaped with

the undercut. For instance, an undercut can be formed from a suitable metal (such as nickel) by depositing a pre-foil layer onto the mandrel, coating the pre-foil with chromium and electrodepositing the main foil on top of the chromium-coated layer. Adhesion to the chromium is poor and the main foil will readily separate from the chromium-plated mandrel. The chromium layer can be passivated with a suitable treatment (for example, dipping in 5% sodium dichromate solution for 10-60 seconds at room temperature), if required. To further assist the separation of the main foil from the pre-foil, it is advisable to have the chromium coated pre-foil firmly attached to the mandrel, so that separation only occurs between the main foil and the pre-foil.

d) Undercuts on Three-Dimensional Foils.

Due to the complex shape of three-dimensional foils, the difficulties experienced in "pre-formed" foils are exacerbated. It is feasible but it may not be easy to remove the pre-foil from the main foil by mechanical separation. The pre-foil can, however, readily be removed by dissolution. Undercuts can also be created in three-dimensional electroforms by using permanent pre-foils on the mandrel as described in c). For simple dissolution the pre-foil must be a different metal to the main foil. The pre-foil is deposited onto the three-dimensional mandrel and if desired, can be passivated. Suitable metals for the pre-foil are copper, tin and zinc and a suitable metal for the main foil is nickel. Copper can be dissolved from nickel by anodic electrochemical dissolution in a solution of 100 g/l penta sodium triphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$ also known as sodium tripolyphosphate) and 30 g/l boric acid (H_3BO_3). The solution operates at 55°C or over and requires a minimum anodic current density of 100 amps per square foot (100

ASF or 120 mA/cm²). Dissolution of the copper can be slow with rates of 1 µm per 5 minutes being experienced.

5 Alternative solutions for the dissolution of copper from nickel include chemical dissolution of the copper in a solution of 175 g/l sodium sulphide and 13 g/l sulphur, or electrolytic anodic dissolution in an electrolyte of 100 g/l sodium sulphide with the application of 2V, or
10 the anodic electrolytic dissolution of copper in a solution of 80 g/l sodium hydroxide and 145 g/l sulphur.

An alternative electrolyte has been used to electropolish copper and it is not reported as attacking nickel; this solution comprises 175 mls water, 825 mls
15 ortho-phosphoric acid (85%) and operates at 18-38°C with an applied voltage of 1.6V.

Tin, zinc or any other easily dissolvable metal or metal alloy can be used in place of copper and can be
20 electrodeposited from either an acid or alkaline electrolyte. The electrodeposited metal can then be dissolved from the nickel electroform by electrolytic or chemical dissolution in an alkaline solution. Both methods allow for the recovery of the electrodeposited
25 metal without affecting the nickel electroform.

As for the apertures in the foil, their size depends on many factors, including their purpose (i.e. shaving or long-hair trimming); how many shaving heads (foils) are present on the
30 razor; foil shape, size and thickness; and whether additional protection is available to limit skin penetration and prevent contact with the blades of the moving undercutter. Selection of aperture size is a compromise; the larger the hole, the more efficient it becomes in 'capturing' both hair
35 (desirable) and skin (undesirable). Unfortunately, the

presence of larger but necessarily fewer holes tends to result in a less efficient cutting performance because of a reduction in the number of aperture bars against which the cutting action occurs. Apertures should therefore be large
5 to accommodate the longest hairs anticipated (say 400 to 600 microns for 24-hour hair growth), but not so large as to result in excessive skin penetration - particularly when foils are thin or worn - or to seriously reduce the number of available cutting events during each stroke of the cutter.

10

More realistically, maximum and minimum aperture dimensions of, say, 2.0 x 0.2 mm would not be unreasonable limits for an irregular shaving aperture pattern, tending towards a
15 diameter of 0.6 mm for more uniform shapes.

For long-hair cutting apertures which are 'protected' to prevent excessive skin penetration, the requirement to restrict size is less critical. Probably the main
20 consideration is to ensure that the aperture width (in the direction of cutter movement) is not so large as to seriously reduce the number of available aperture bars which, in conjunction with the cutter blades, provide the cutting action. Thus the minimum aperture dimension is likely to be
25 similar to that for a normal shaving aperture, but apparent length could be in excess of 2.0 mm.

Once the electroform has been produced to the required thickness, the three-dimensional metal shape can be readily
30 removed from the mandrel. The passivation pre-treatment process facilitates this operation.

Benefit can be obtained by using a mandrel that has a coefficient of expansion which differs from that of the
35 electroforming metal. Once the electroform has been

produced, removal can be facilitated by exposing the electroform and mandrel, in situ, to either heat or cold, with the differing rates of expansion or contraction assisting in the parting of the electroform from the mandrel.

5

The thickness distribution can be modified and improved if desired by the use of robbers for equalising the current density distribution during electroforming.

- 10 The success of three-dimensional electroforming is dependent on producing a suitable mandrel and on the production of a suitable mask. The mask will have bar width less than that of the final product. Moreover, the mask must be readily removable from the mandrel. For relatively simple three-
- 15 dimensional shapes conventional photographic artwork can be used as the mask, but if the shape is complex, it is not possible to fold or bend this artwork to the required shape. In such cases the mask may be formed in a pliable metal, preferably copper, silver, gold, platinum, palladium,
- 20 bismuth, cadmium, indium, lead, thallium, tin or zinc, and then bent, drawn or otherwise mechanically formed to the required shape. This will be described hereinafter. However, provided a mask can be developed which is both accurate and impervious to ultraviolet light, other types of mask (e.g.
- 25 paint or inks) could be used, or a polyester mask could be produced by vacuum forming over a mandrel.

- The production of a copper mask, described below, is an easy and successful method of obtaining a patterning tool which
- 30 offers the advantages of being durable and reusable. Copper or other similarly ductile metals are preferred for the formation of the mask as they can be easily fashioned into the required three-dimensional shape. Care must be taken in designing the mask to take account of any extraneous growth
- 35 of the electroform, compared to the dimensions of the mask,

that may occur if the electroform is thicker than the resist coating.

The nickel electroform can be successfully produced using the
5 three-dimensional electroforming process without loss of
replicated pattern detail, strength or dimensional accuracy.
It should be noted that if it is desired to produce an
aperture of predetermined dimensions in the final
electroform, e.g. a hair-capture aperture in a shaving foil,
10 the corresponding aperture in the mask has to be made
somewhat larger than the required final dimensions. When
making a shaving foil, it is found that the mask apertures
should be about 200 μm larger than the desired dimension of
the final product. For example, to produce a shaving foil
15 aperture of diameter 600 μm a mask aperture diameter of 800
 μm would be required.

Example 1

20

To make a rotary shaving foil as shown in Fig. 6, the
following specific steps were used.

Before coating a mandrel with electrophoretic photoresist,
25 the following pre-treatment steps were used:

- 1) Clean the mandrel by rubbing with a slurry of abrasive
chalk ("Sturcal"™).
- 2) Thoroughly rinse with running water.
- 30 3) Dip in a cold (20-30°C, preferably 20°C) acid cleaner
for 15-180 seconds, preferably 30 seconds, to remove any
residual chalk. A 10% (v/v) solution of sulphuric acid
is suitable.
- 4) Rinse with deionised water for 20 seconds.
- 35 5) Dip in alkaline cleaner ("Neutraclean"™) for 60-180
seconds at 20-65°C, preferably, 120 seconds at 60°C.

- 6) Thoroughly rinse in deionised water for 30 seconds.
- 7) Dip in cold acid cleaner (20-30°C, preferably 20°C) for 15-180 seconds, preferably 30 seconds. A solution of 10% (v/v) sulphuric acid is suitable.
- 5 8) Thoroughly rinse with deionised water for 30 seconds.
- 9) Clean by immersing in rinsing agent, e.g. "Rinse Aid"TM for 60-180 seconds at 40-50°C, preferably 120 seconds at 45°C.
- 10 10) Dip in "Permeate Rinse"TM for 60-180 seconds at 40-50°C, preferably 120 seconds at 45°C.

The photoresist was then applied using the apparatus of Fig. 2 as follows:

- 15 11) Dip the mandrel in "PCR 3000"TM photoresist at 20-60°C, preferably 23-28°C, e.g. 25°C; leave to soak for about 60 seconds, then apply 30V for 45 seconds.
- 12) Dip in "Permeate Rinse"TM for 60-180 seconds at 40-50°C, preferably 2 minutes at 45°C.
- 20 13) Dip in "Rinse Aid"TM for 60-180 seconds at 40-50°C, preferably 2 minutes at 45°C.
- 14) Rinse with deionised water for 30 seconds.
- 15) Dry in oven at 60-80°C for 10-15 minutes, preferably 25 75°C for 10 minutes.

These steps produce a nominal photoresist thickness of 8 μm .

- Following exposure of the photoresist for about 4 minutes in the manner described with reference to Fig. 3, the mask and cap were removed. The time of exposure is of course dependent on the power of the lamp 31. Using a wavelength of 365 nm, an exposure of 1350 mJ/cm² is required in this example. The photoresist was then developed using the apparatus of Fig. 4 as follows:
- 30
- 35

- 1) Immerse the mandrel 1 in "Developer" 41 held in an insulated heated tank 43 at 20°C-50°C, preferably 26°C-29°C until the pattern is just visible; note the time
5 taken and continue the immersion for the same period. A period of 70-100 seconds usually suffices.
- 2) Thoroughly rinse the mandrel and photoresist with deionised water.
- 3) Cure the photoresist at 160°C-200°C for 20-30 minutes,
10 preferably 200°C for 30 minutes.
- 4) Allow to cool.

During the developing step, the developer was agitated with the stirrer 42.

15

Once developed, the mandrel with its layer of photoresist was subjected to passivation treatment as follows:

- 1) Gently abrade with a slurry of "Sturcal"™ chalk.
- 20 2) Rinse in running water.
- 3) Immerse in cold acid cleaner for 15-180 seconds at 20-30°C, preferably 30 seconds at 20°C. A 10% (v/v) solution of sulphuric acid is suitable.
- 4) Rinse in deionized water.
- 25 5) Soak in cold (room temperature) alkaline cleaner for 2 mins.
- 6) Rinse in deionized water.
- 7) Immerse in cold acid cleaner for 15-180 seconds at 20-30°C, preferably 30 seconds at 20°C. As above, a 10%
30 (v/v) solution of sulphuric acid may be used.
- 8) Rinse in deionized water.
- 9) Immerse in a 5% potassium dichromate solution for 15 seconds.
- 10) Rinse in water.

- 11) Thoroughly rinse in running deionized water for a minimum of 45 seconds.

Following pretreatment, a nickel layer was electroformed onto the mandrel using the apparatus of Fig. 5 with a nickel sulphamate electroforming solution operating at a typical current density of $35\text{-}40\text{mA/cm}^2$. Electroforming was carried out with an applied current of 155 mA for 2 hours to produce a electroform thickness of about $90\mu\text{m}$.

10

During electroforming, the operating temperature of the nickel sulphamate solution should not exceed 70°C , and preferably should be about 60°C , in order to prevent the sulphamate ions dissociating into sulphate and ammonium ions. The ammonium ions would introduce stress into the deposit.

Fig. 6 shows a cross-section through the final nickel electroformed product 60. As shown, the product has a flat central area 21 with a central aperture 22. The flat central area 21 passes through a vertical link portion 24 to a foil area 23 which merges into a outer rim 25. The thickness of the foil in the flat central area is in the region of $75\mu\text{m}$, about $70\mu\text{m}$ in the vertical link area 24, and around $90\mu\text{m}$ in the foil area and outer rim.

25

As illustrated in Fig. 6, the thickness distribution of metal across the final electroform 60 is quite symmetrical about the vertical axis, with the foil region of the component showing an average thickness of about $85\mu\text{m}$, whilst the outer rim has an average thickness of about $90\mu\text{m}$ to $93\mu\text{m}$. The central flat area has a thickness of about $75\mu\text{m}$ although this diminishes to about $43\mu\text{m}$ as the central hole is approached. The vertical area linking the foil area to the central flat region has an average wall thickness of about $70\mu\text{m}$. This ratio of thicknesses can be easily maintained without the use

of robbers to modify the current density distribution over the mandrel. However, if changes in the current distribution are required, they can easily be achieved by the use of robbers. It will be appreciated that the central hole in the electroform is used as a locating point in the final assembly and is formed by the use of the insert plug 5 shown in Fig. 1.

The method used for the formation of the mask is illustrated in Figures 7 to 10.

Initially a polyvinyl alcohol-based liquid photoresist or another suitable photoresist is deposited onto a flat stainless steel plate and processed to form the required pattern. This is achieved by exposing the coated plate to light through photo tooling artwork of the required pattern. The photoresist is then developed and processed.

The mask is then electroformed for about 45 minutes from a low stress dull acid copper solution operating at 35A/ft^2 and at room temperature. This produces a mask with a nominal thickness of $40\mu\text{m}$ which has sufficient inherent strength to enable easy handling whilst still being malleable. It is important that the copper should be as ductile and stress-free as possible.

Shaping of the flat copper electroform into a three-dimensional mask is achieved by pressing it with drawing tools made from synthetic plastics materials. Referring to Fig. 7, the flat electroformed copper member 31 is pressed between a male pressing member 32 and a female pressing member 33 to produce the preform 141 shown in Fig. 8. The preform of Fig. 8 is then pressed in the second pressing tool shown in Fig. 9 to produce the final mask 3 shown in Fig. 10. The pressing tool of Fig. 9 comprises a first member 52 the

surface of which defines the flat central region of the mask, and a second member 53 having a conical wall portion 54 for shaping the outer rim of the mask. The first member 52 is supported on a coil spring 55 for reciprocation relative to the second member 53. The pressing tool comprises a third portion 56 having a conical male portion 57 which co-operates with the conical recess 54 of the second portion 53 to shape the outer rim of the mask.

A third tool, not illustrated, is used to trim any waste material from the outer rim. It is essential that the shaping of the mask is carried out in multiple stages because the stresses exerted during drawing and forming would otherwise be sufficient to tear the copper especially in areas of fine detail.

Example 2

Although it is conventional to produce shaving foils in a flat condition, when in use a shaver foil usually has a curved shape conforming to that of the undercutter. Producing a shaver foil in the curved condition enables the foil to conform better to the profile of the undercutter. This increases the effectiveness of shaving.

The following technique is applicable to produce shaver foils of various shapes and configurations.

A foil pattern mask is first made by the follow steps:

- a) Mechanically brush the surface of a stainless steel plate mandrel to have a surface roughness of less than 0.1μ inches centre line average.
- b) Rinse the mandrel in deionised water for 30 seconds.

- c) Dip the mandrel in a hot alkaline cleaner (e.g. "Neutriclean"TM) at 20-65°C for 60-180 seconds, preferably 60°C. for 2 minutes.
- d) Rinse the mandrel for 30 seconds.
- 5 e) Dip the mandrel in a cold acid cleaner for 15-180 seconds at 20-30°C, preferably 1 minute at 20°C.
- f) Rinse the mandrel for 30 seconds.
- g) Dip the mandrel in "Rinse Aid"TM at 40-50°C for 60-180 seconds, preferably 40°C for 2 minutes.
- 10 h) Dip the mandrel in "Permeate Rinse"TM at 40-50°C for 60-180 seconds, preferably 40°C for 1 minute.
- i) Soak the mandrel in "PCR 3000"TM electrophoretic photoresist at 20-60°C, preferably at 25°C for 60 seconds.
- 15 j) Apply a potential of 30V at 30A for 45 second. (Note the current falls to about 0.0-0.2A during this procedure.)
- k) Dip the mandrel in "Permeate Rinse"TM at 40-50°C for 60-180 seconds, preferably 40°C for 1 minute.
- 20 l) Dip the mandrel in "Rinse Aid"TM at 40-50°C for 60-180 seconds, preferably 40°C for 2 minutes.
- m) Rinse the mandrel in deionised water for 30 seconds.
- n) Dry in an oven at 60-80°C for 10-15 minutes, preferably 75°C for 10 minutes.
- 25 o) Allow the mandrel to cool.
- p) Expose the coated mandrel through photo-tooling artwork to UV radiation at 365 nm for sufficient time to achieve 1350 mJ/cm².
- q) Develop the mandrel pattern in "Developer"TM at 20-50°C, preferably 26°C. until the aperture pattern is just visible; note the time taken and continue the immersion for the same period.
- 30 r) Thoroughly rinse the mandrel and photoresist. with deionized water.

- s) Cure the photoresist at 160-200°C for 20-30 minutes, preferably 200°C for 30 minutes.
- t) Allow to cool.
- u) Clean the mandrel by rubbing with a slurry of abrasive chalk (e.g. "Sturcal"TM).
- 5 v) Rinse the mandrel in deionized water for 30 seconds.
- w) Soak the mandrel in cold acid cleaner as in step e).
- x) Rinse the mandrel in deionized water for 30 seconds.
- y) Soak the mandrel in an alkaline cleaner (e.g. "Neutracleam"TM) as in step c).
- 10 z) Rinse the mandrel for 30 seconds in deionized water.
- a1) Dip the mandrel in a cold acid cleaner as in step e).
- b1) Rinse the mandrel in deionized water for 30 seconds.
- c1) Electroform the pattern in copper from a dull acid electroplating solution comprising:
- 15 200g/l copper (II) sulphate
 10g/l copper (II) chloride
 30 ml/l sulphuric acid (SG 1.84)
 at room temp with a Cathodic Current density of 55mA/cm²
- 20 for a time of 40 minutes.
- d1) Rinse the electroform in deionized water for 30 seconds.
- e1) Peel off the electroform from the stainless steel mandrel.

25 Steps g) to s) can be modified by using conventional liquid polyvinyl alcohol photoresist.

A polished mandrel is prepared for the application of electrophoretic photoresist as described in steps c) to o)
30 above.

The mask is mounted in a Perspex cap and is then applied to the photoresist coated mandrel and the whole is exposed to UV light for sufficient time to thoroughly expose the

photoresist to the light. It is then processed according to above steps q) to t).

The mandrel with its layer of developed photoresist is prepared for electroforming as described in steps u) to b1). Separation of the final electroform from the mandrel can be facilitated by the inclusion of dipping, either chemical or electrochemical, in a solution of a soluble dichromate salt or another suitable oxidising solution. Electroforming of the head is carried out in a nickel sulphamate solution. Electroforming is carried out in a nickel sulphamate bath at 60°C and a cathodic current density of 30-60 mA/cm² for 90 to 180 minutes. The electroform can then be removed from the mandrel and mounted onto an undercutter assembly to form a shaving system.

Example 3

The invention may also be applied to the manufacture of filigree patterns suitable for decorating writing instruments.

Thus, a pattern can be electroformed which can be used to impart a decorative finish onto articles such as fountain pen barrels.

The method of manufacture entails the creation of a mandrel conforming to the shape of the pen barrel and a required artwork mask. The artwork mask is held in close contact with the photoresist coated mandrel by a split perspex casing or "astragal" and the photoresist is exposed to a suitable source of electromagnetic radiation to produce an image in the photoresist. This image is used to produce the electroform. To assist in the removal of the electroform from the mandrel it may be beneficial if the mandrel and

electroforming metal have significantly different coefficients of expansion; this difference in properties can be used to release the electroform from the mandrel by exposing the mandrel, with the electroform in situ, to either
5 heat or cold with the result that the electroform will become detached from the mandrel.

The artwork mask can be produced by the technique described above in connection with Example 2, or by any of the
10 techniques described below in connection with Figs. 11 to 19 of any of the other described techniques not specifically illustrated.

The following alternative methods of creating a mask are
15 possible:

a) Electroform a blank mask to the required thickness on either a permanent or disposable mandrel. Etch or cut the pattern from the blank by using a suitable laser
20 source, thus creating the required pattern. Suitable types of laser include YAG, CO₂, Copper Vapour and Excimer. The type of laser used to prepare the mask pattern depends on the level of definition in the mask. A CO₂ laser produces only a very coarse pattern, a YAG
25 laser will only produce a coarse definition, whilst Copper Vapour lasers can produce fine patterns. Excimer lasers can produce even finer definitions. Consequently, the type of laser suitable for preparing patterned masks depends on the quality of pattern definition required in
30 the final product. For preparing masks for electric razor foils, the best laser is Excimer, whilst Copper Vapour may be able to offer adequate definition, although the required definition for a razor foil mask is on the current limit of that available by Copper
35 Vapour technology. If coarser pattern definition is

adequate, as in the preparation of masks for pen barrel patterning, other lasers, such as CO₂ and YAG can also be used.

- 5 b) As shown in Figs. 11 to 13, electroform a sufficiently thick metal blank 112 of the mask on a suitable mandrel and machine the required pattern into the blank metal using a Computer Numerically Controlled (CNC) machine 121. The mandrel 111 may be either permanent or
10 disposable. If the base material of the mandrel is non-conducting, the mandrel must be metallised prior to electroforming the blank mask. The patterned mask is shown in Fig. 13.
- 15 c) As shown in Figs. 14 to 16, metallise a plastic mandrel 141 with a thin layer 142 of a suitable metal, such as copper or silver and etch the required pattern from the metal film by using a suitable laser 151. The mandrel must be carefully oriented and manipulated on a multi
20 axis (5 or 6 axis) engineering table to ensure that the etching electromagnetic radiation only strikes the mandrel normally, otherwise definition is jeopardised. The pattern is then thickened by electroforming to produce the mask of the required thickness. As in method
25 a), suitable types of laser may include YAG, CO₂, Copper Vapour and Excimer. The plastic mandrel 141 is then dissolved away to leave the mask 161 shown in Fig. 16.
- 30 d) Coat a metal mandrel with a non-conducting material and ablate the pattern from this coating. The mandrel must be carefully oriented and manipulated on a multi axis (5 or 6 axis) engineering table to ensure that the
35 ablating electromagnetic radiation only strikes the mandrel normally, otherwise definition may be

jeopardised. The mask is then electroformed on the mandrel to the required thickness. Since only non-conducting material is ablated from the coating, the best suited currently available laser is the Excimer.

5

e) As shown in Figs. 17 to 19, the pattern 181 of the mask may be printed onto a mandrel 171 with a conducting surface (i.e. the mandrel can be either metal or a metallised non-conductor). The print medium can be
10 either a suitable printing ink or resist and can be applied with a tampo printing pad 182. The mask can then be electroformed to the required thickness on the patterned conducting mandrel, as shown in Fig. 19.

15

f) An opaque (to UV) plastic material may be vacuum-formed over a mandrel conforming to the desired shape of the mask. This results in a free standing shell which is used as the basis for the mask. This shell is mounted
20 on a jig for multi axis manipulation in conjunction with an excimer laser. The laser directly ablates the desired pattern onto the plastic shell resulting in a free-standing plastic mask. This process eliminates the need for a mask electroforming stage and thus makes
25 redundant the foil aperture size compensation required for the above-described techniques. The plastic material is preferably 100-200 microns thick polyester.

Alternatively, as shown in Fig. 22, a mask 221 may be made
30 directly a flat two-dimensional photo tooling artwork 222, which can be bent around the internal circumference of the astragal 223. If the phototooling artwork is used as the mask, the photographic emulsion should be in contact with the photoresist. The two halves of the astragal are held together
35 by retaining rings at each end of the assembly.

If the mask is electroformed as a two-dimensional form by the method given in Example 2 and is sufficiently robust, it can be removed from the plate mandrel by the application of
5 adhesive tape. By carefully lifting the tape with the patterned mask attached, the mask can be removed from the plate and be more easily handled. Separation of the mask from the tape can be achieved by using a suitable solvent such as a mixture of 70% (vol.) propan-2-ol and 30% acetone.
10 Using 100% acetone results in the swelling of the backing of the adhesive tape and the copper mask distorting.

A stainless steel mandrel can be prepared as described above in connection with Example 2. Electrophoretic photoresist
15 can be applied to the mandrel by techniques similar to those described above.

If the mandrel is brass, as may be used for electroforming nickel and using thermal separation techniques, it is
20 advisable to coat the brass with not less than 5 μm of nickel to provide a good release surface. To minimise the risk of damage to the photoresist pattern, the mandrel can be "built up" to the thickness of the photoresist by depositing metal such as nickel or copper, to the thickness of the
25 photoresist. This results in the surface layer of the mandrel being of uniform thickness.

Prior to producing the final electroform, the mandrel, if nickel plated, must be passivated with a suitable surface
30 pretreatment such as dipping it in a solution of 200 g/l sodium metabisulphite or other treatments such as a powerful oxidant (e.g. sodium dichromate). These treatments can be either chemical or electrolytic.

Electroforming is carried out as described above in conjunction with Example 2.

In the example described, electroforming was carried out in 5 nickel sulphamate at 60°C with an applied cathodic current density of 54 mA/cm² for 200 minutes.

For use in any of the above Examples 1 to 3, the following materials may be obtained from the sources indicated:

10

Material	Source
1) Neutraclean™	ShIPLEY Co.
2) Rinse Aid™	Surcotech Ltd.
3) Permeate Rinse™	Surcotech Ltd.
4) PCR 3000™	Surcotech Ltd.
5) Developer	Surcotech Ltd.
6) Sturcal™	Rhone Poulenc.

Neutraclean™ is a trade name for essentially a solution of sodium metabisulphate in water.

- 5 Permeate Rinse™ is a trade name for an emulsion stabilizer containing lactic acid.

- 10 PCR 3000™ (sometimes known as PCT 3000™) is a trade name for an electrophoretic photoresist containing 1-methoxy-2-propanol ethylene glycol n-hexyl ether, acetone and lactic acid.

"Developer" is the developer supplied by the manufacturer of PCR 3000™ for use with that photoresist.

15

Sturcal™ is a trade name for ultrafine precipitated calcium carbonate.

- 20 The materials 2-5 in the above list are manufactured by LVH Coatings Ltd., of Coleshill, Birmingham, U.K., but are currently available from Surcotech Ltd., as noted above.

Claims:

1. A method of producing an electroformed article in which:
 - a) a coating of electrophoretic photoresist is applied
 - 5 to a substrate having an electrically conductive surface by passing an electrical current therethrough;
 - b) the photoresist is exposed to a suitable source of electromagnetic radiation through a mask whose shape conforms closely to that of the substrate;
 - 10 c) the photoresist is developed; and
 - d) a metallic layer is electrodeposited onto the conductive surface regions of the substrate not coated with the photoresist.
- 15 2. A method according to claim 1, in which the substrate is of stainless steel.
3. A method according to claim 1 wherein the substrate is a body of plastics material having an electrically conductive
- 20 surface coating.
4. A method according to claim 1, 2 or 3, in which the substrate has non-zero Gaussian curvature.
- 25 5. A method according to any one of the preceding claims in which the mask is provided with a plurality of non-elongate apertures.
6. A method according to claim 5 wherein the apertures each
- 30 have a diameter in the range 600 to 800 microns.
7. A method according to any one of the preceding claims, wherein the mask is provided with a plurality of elongate apertures.

8. A method according to claim 7 wherein the apertures have a length of 400 to 2200 μm and a width of 400 to 800 μm .

9. A method according to any one of the preceding claims in
5 which the metallic layer has a varying relief pattern.

10. A method according to any preceding claim, in which the mask is of ductile metal, e.g. copper.

10 11. A method according to any one of the preceding claims in which the metallic layer is separated from the substrate by peeling or by dissolution of the substrate.

12. A method of manufacturing a three-dimensional
15 electroforming mask for use in the method of any one of the preceding claims comprising the following steps:

- a) applying a photoresist to a flat surface;
- b) patterning the photoresist by exposure and development steps;
- 20 c) electrodepositing a mask preform on the flat surface; and
- d) pressing the preform into the desired three-dimensional shape.

25 13. A method of manufacturing a three-dimensional electroforming mask for use in the method of any one of claims 1 to 11 comprising the following steps:

- a) applying a metallic coating to a substrate; and
- b) patterning the coating by etching using a laser.

30

14. A method according to claim 13 wherein the coating is applied by electroforming to a desired thickness.

15. A method according to claim 13 in which step b) is
35 followed by a thickening step using electroforming.

16. A method according to claim 14 or 15 in which the substrate is removed from the coating.

5 17. A method of producing an electroformed article substantially as hereinbefore described with reference to Figures 1 to 6, 11, 12, 14, 15, 17, 20 and 21 of the drawings.

10 18. A method of manufacturing a three-dimensional electroforming mask substantially as hereinbefore described with reference to Figures 7 to 10, 13, 16, 18 and 22 of the accompanying drawings.

15 19. An electroformed article produced by the method of any one of claims 1 to 11 and 17.

20. An article according to claim 19 wherein the article is a shaving cutter.

20

21. An article according to claim 19 wherein the article is a decorative member conforming to the shape of a pen barrel or cap.

ABSTRACT

**Methods of Electroforming Complex
Three-Dimensional Shapes**

5

A method of producing an electroformed article (60) in which:

- 10 a) a coating of electrophoretic photoresist is applied to a substrate having an electrically conductive surface by passing an electrical current therethrough;
- b) the photoresist is exposed to a suitable source of electromagnetic radiation through a mask whose shape conforms closely to that of the substrate;
- c) the photoresist is developed; and
- 15 d) a metallic layer is electrodeposited onto the conductive surface regions of the substrate not coated with the photoresist. The substrate may be of stainless steel, or of plastics material having an electrically conductive surface coating. The method is applicable to the production
- 20 of articles whose surface has non-zero Gaussian curvature. To produce an apertured electroformed article, the mask is provided with a plurality of apertures, which may be circular or elongate. Methods of producing the mask are also described.

25

(Fig. 6).

30

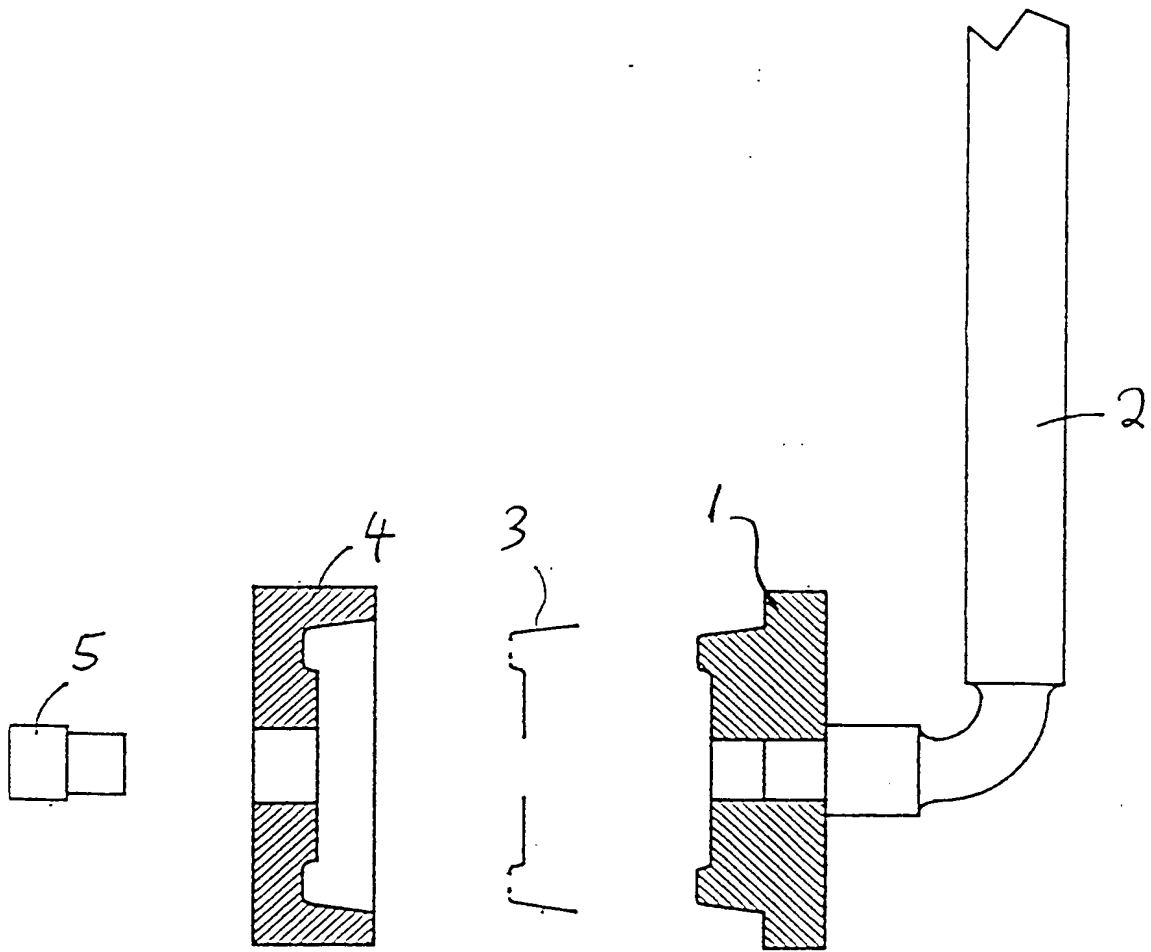


Fig. 1

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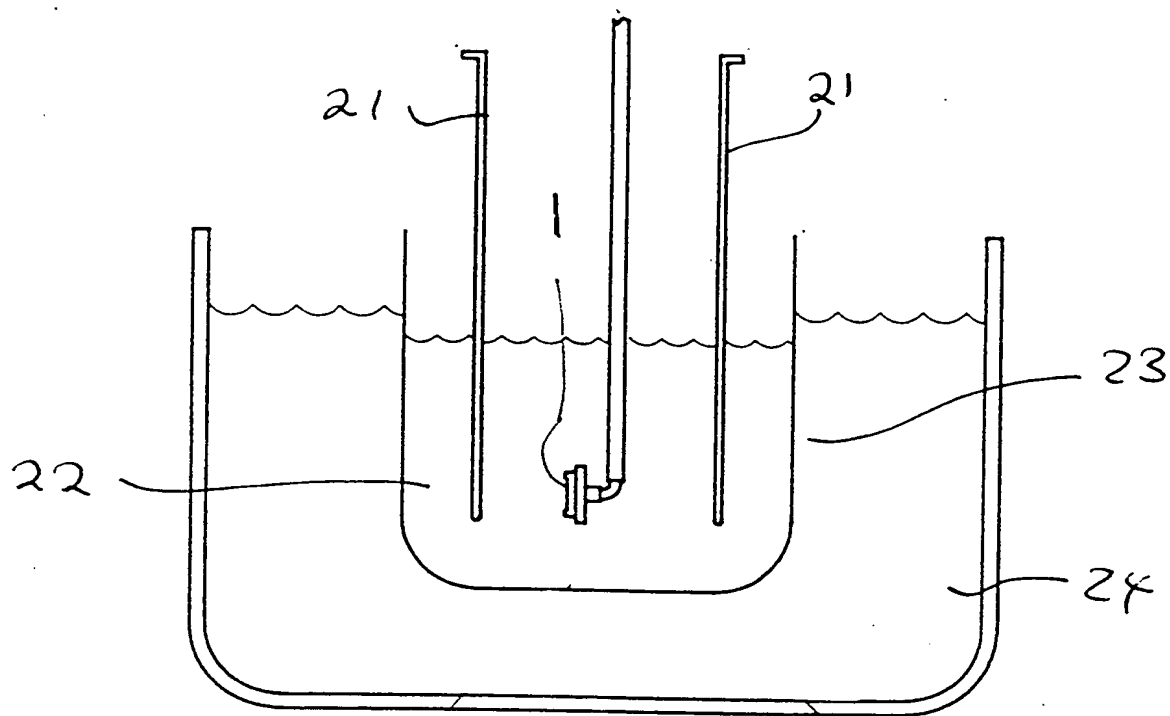


Fig. 2

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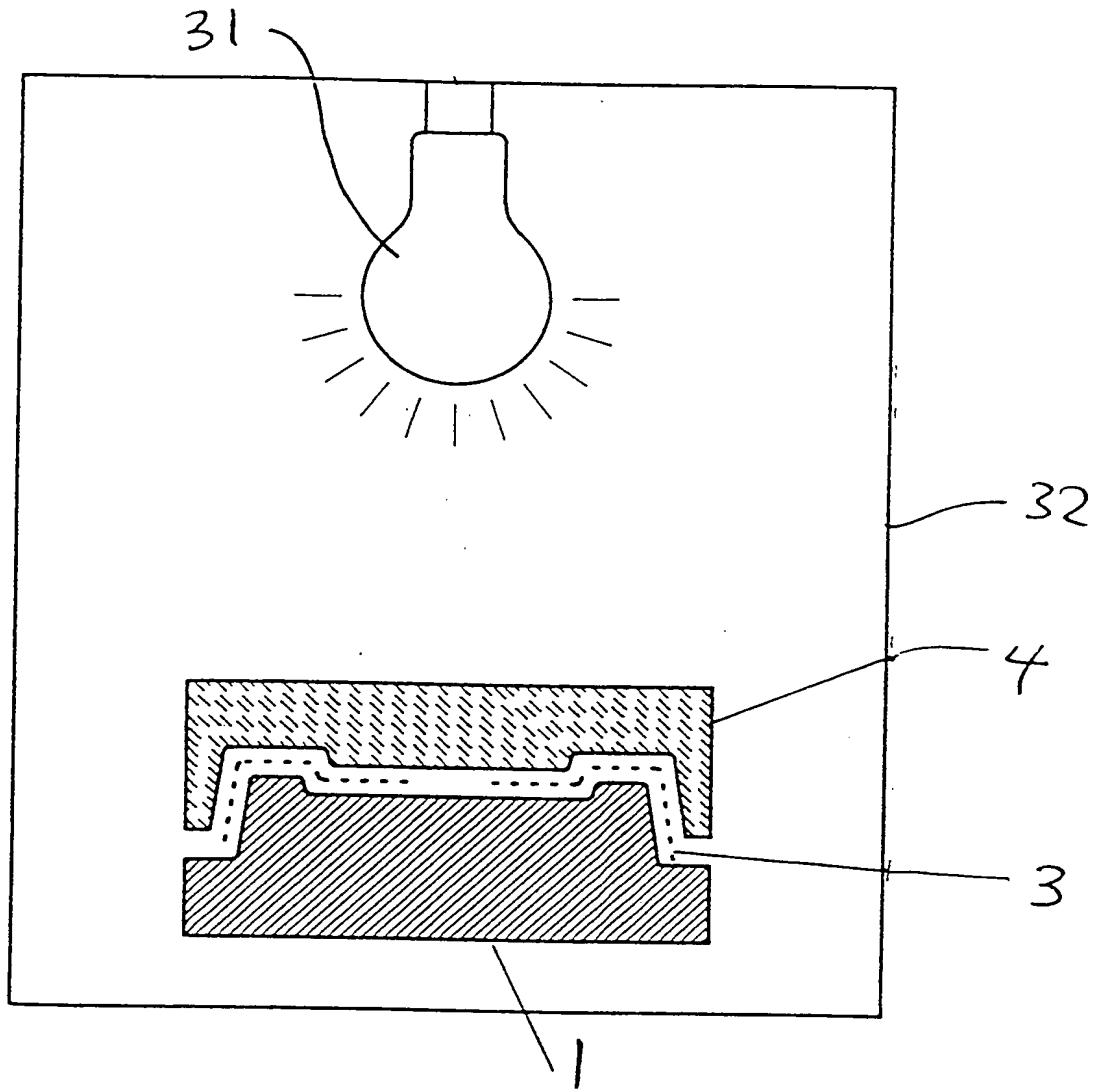


fig. 3

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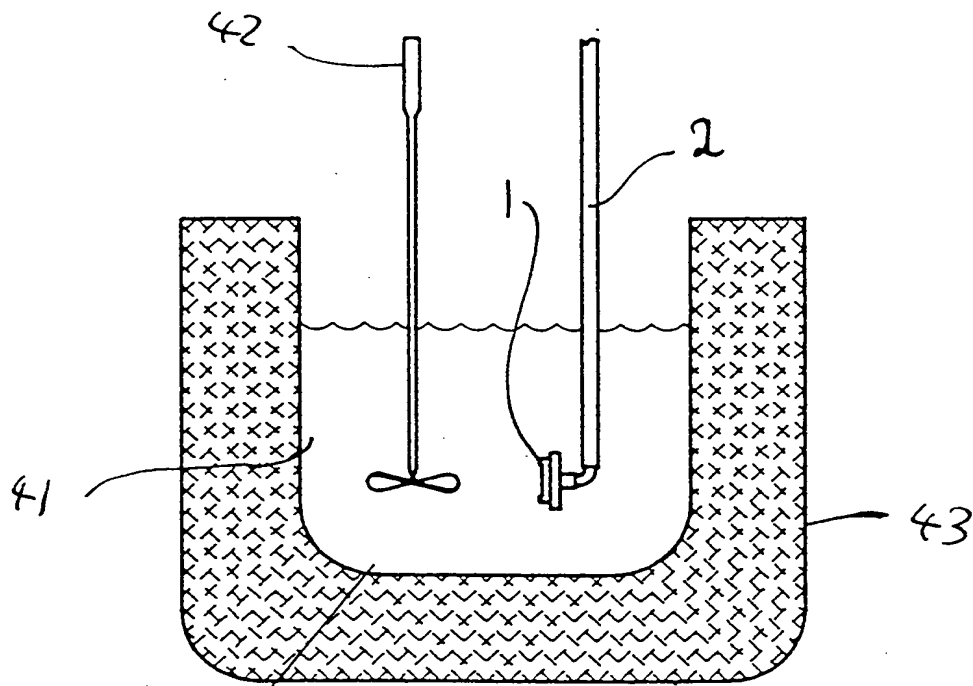


Fig. 4.

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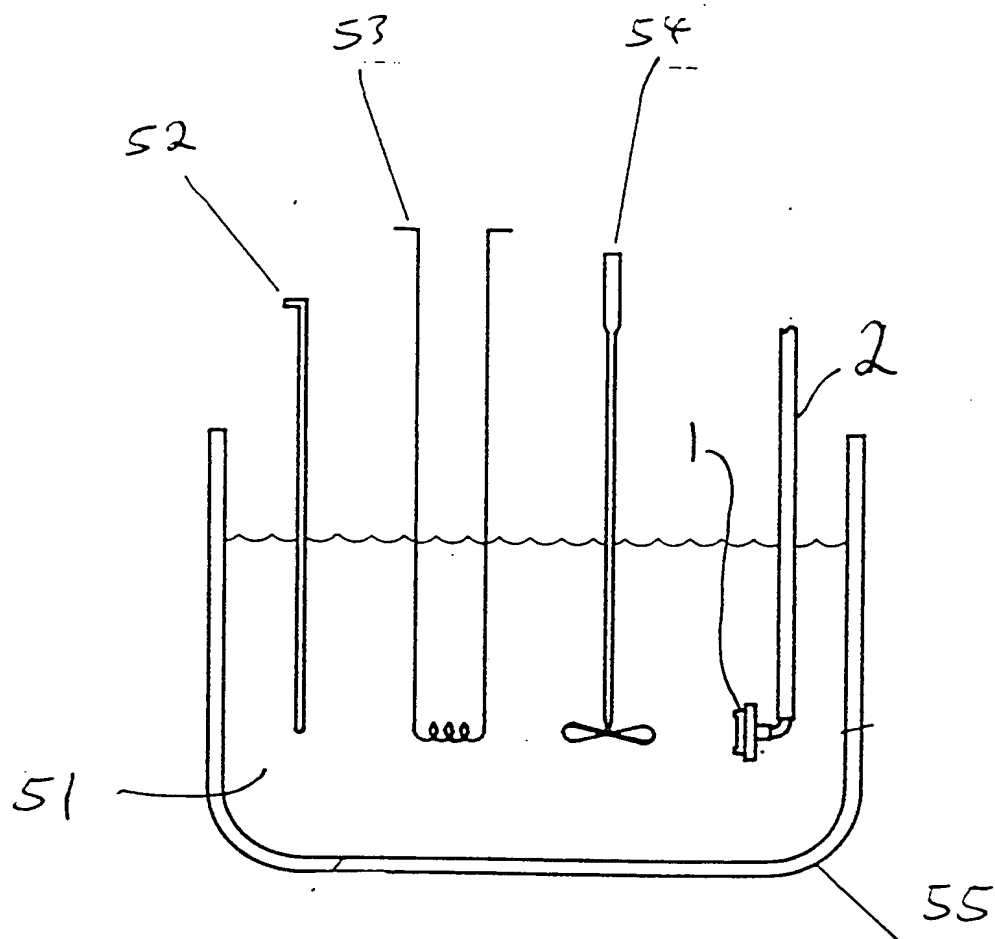


Fig. 5.

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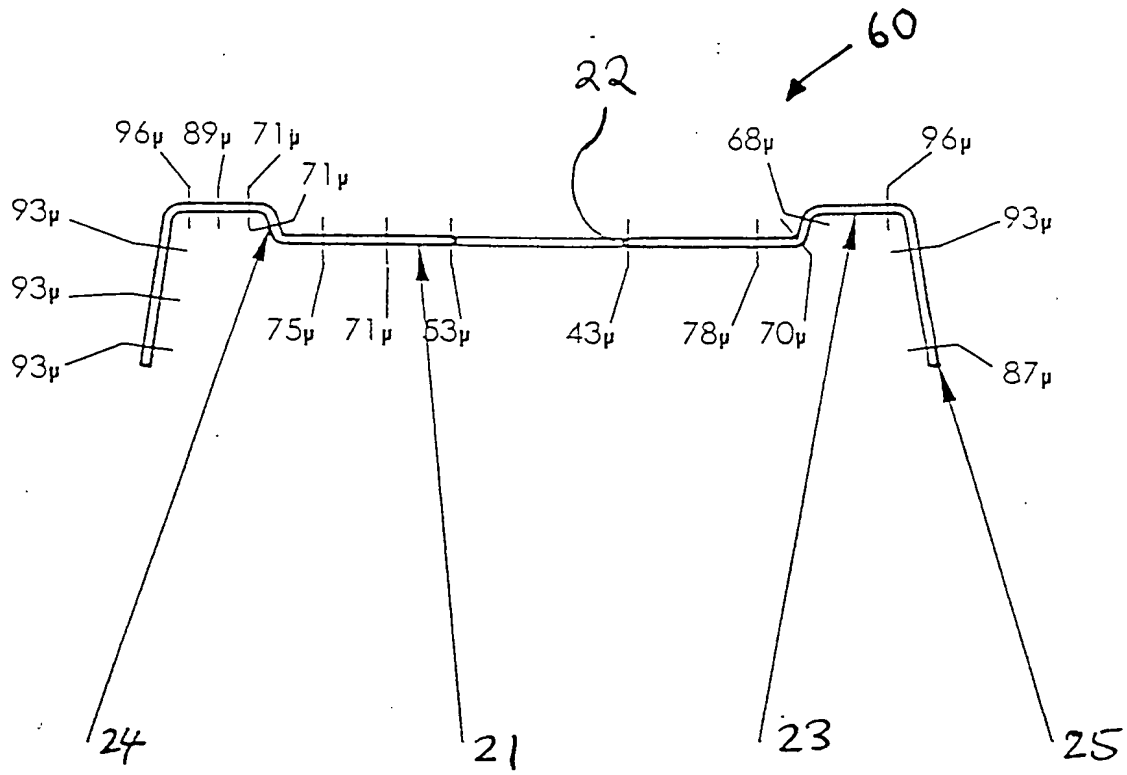


Fig .6

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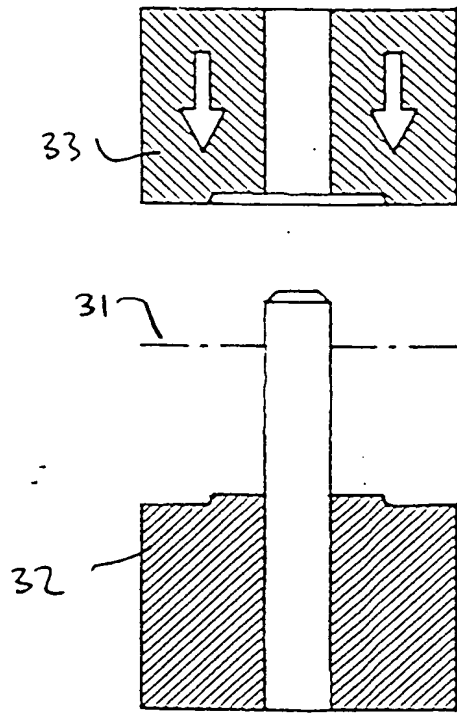


Fig. 7

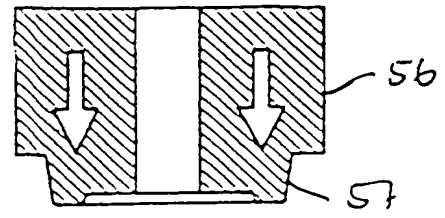


Fig 9

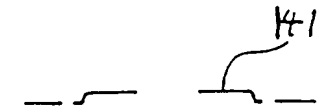


Fig 10

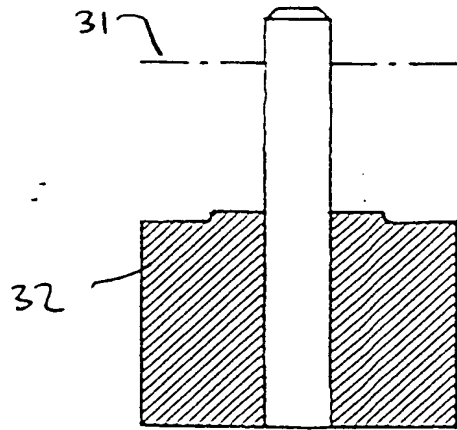
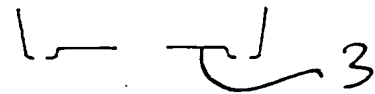
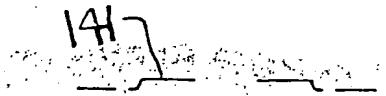


Fig 8



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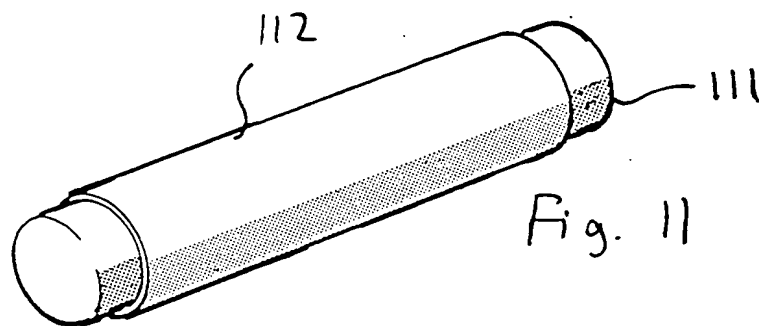


Fig. 11

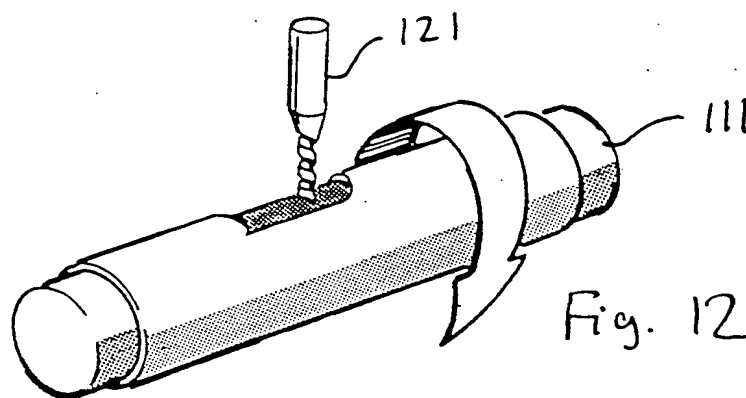


Fig. 12

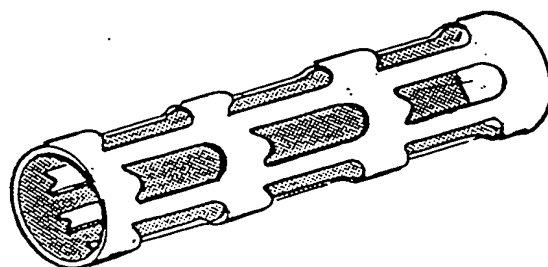


Fig. 13

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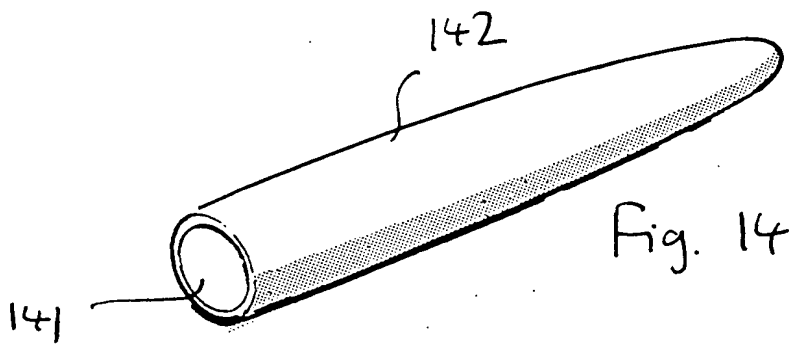


Fig. 14

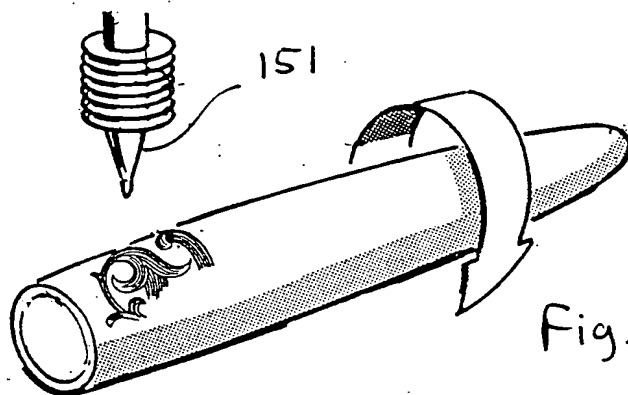


Fig. 15

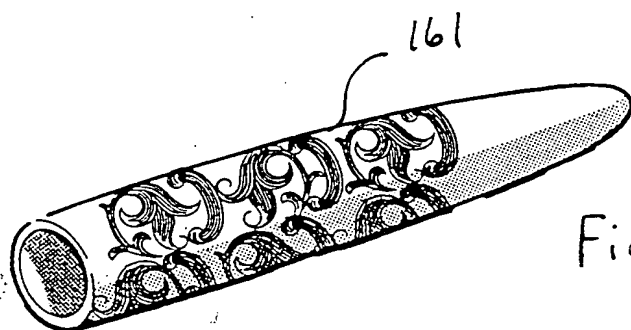
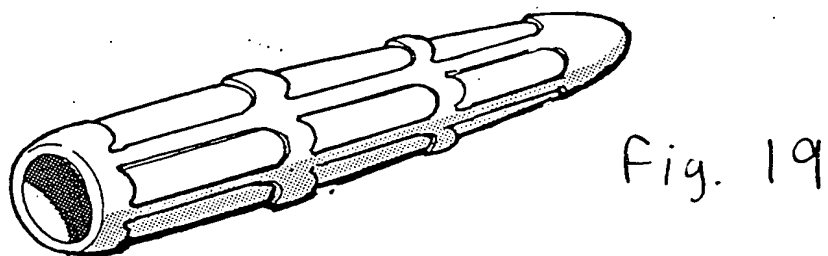
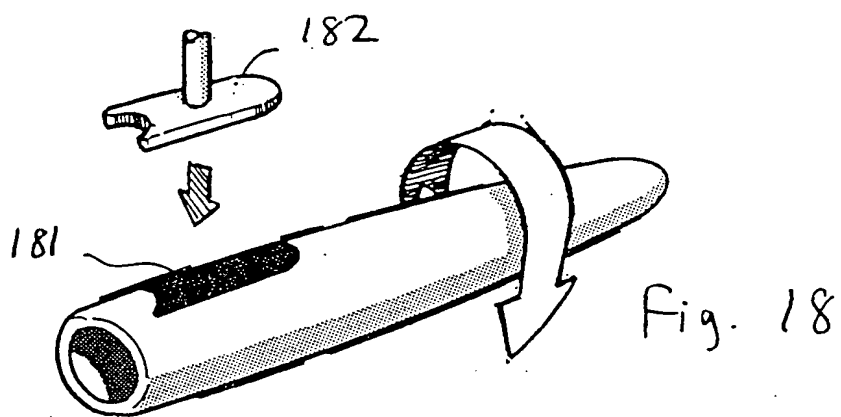
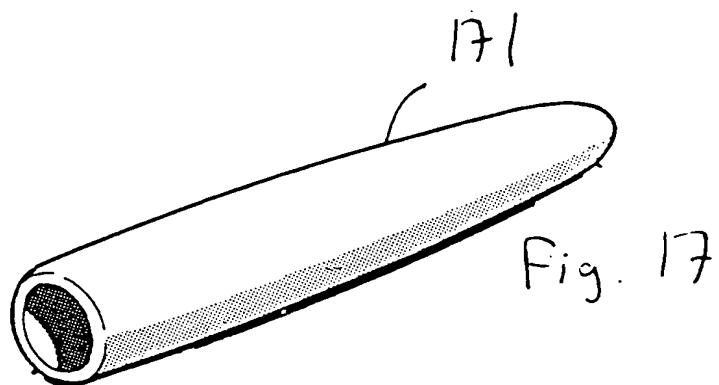


Fig. 16

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Fig. 20

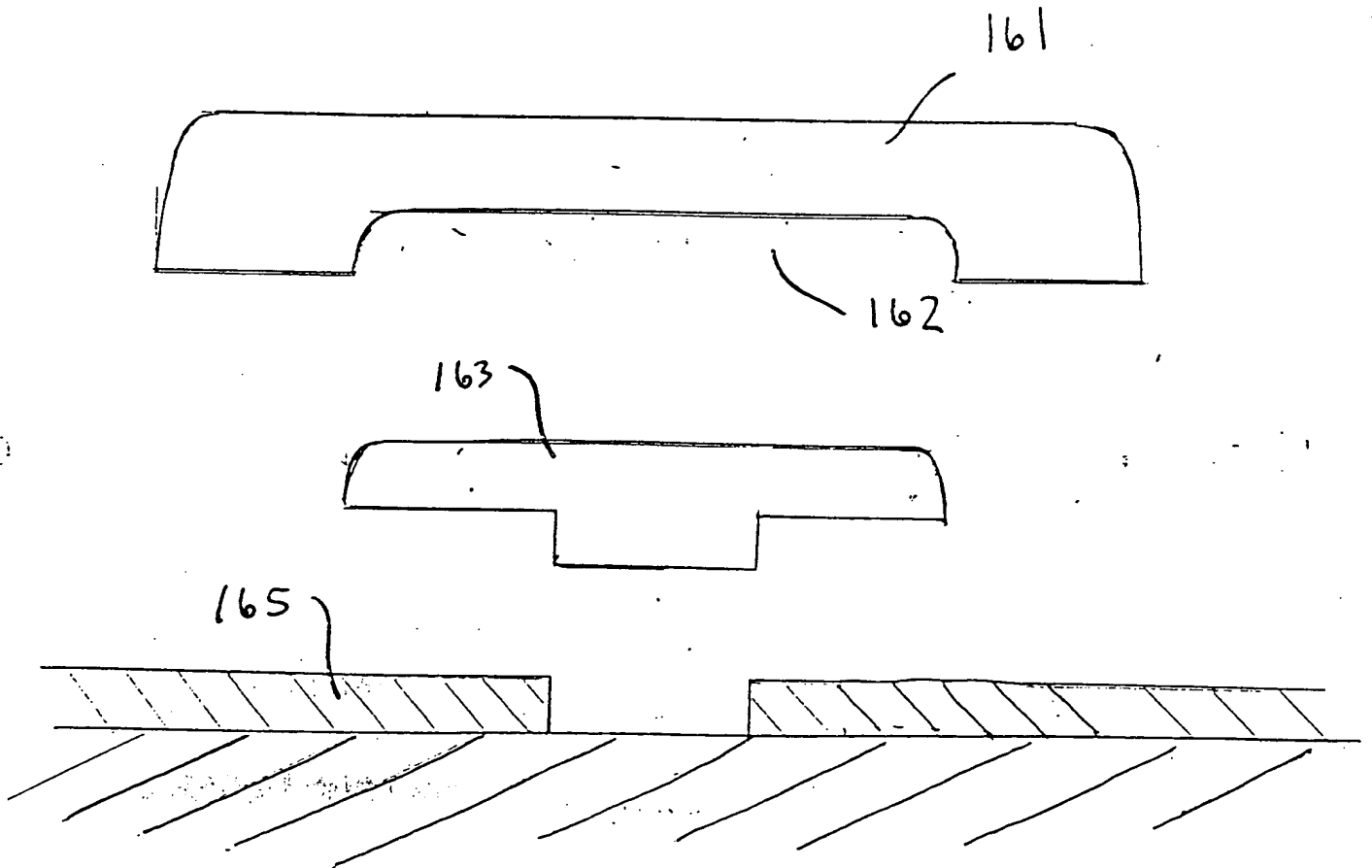
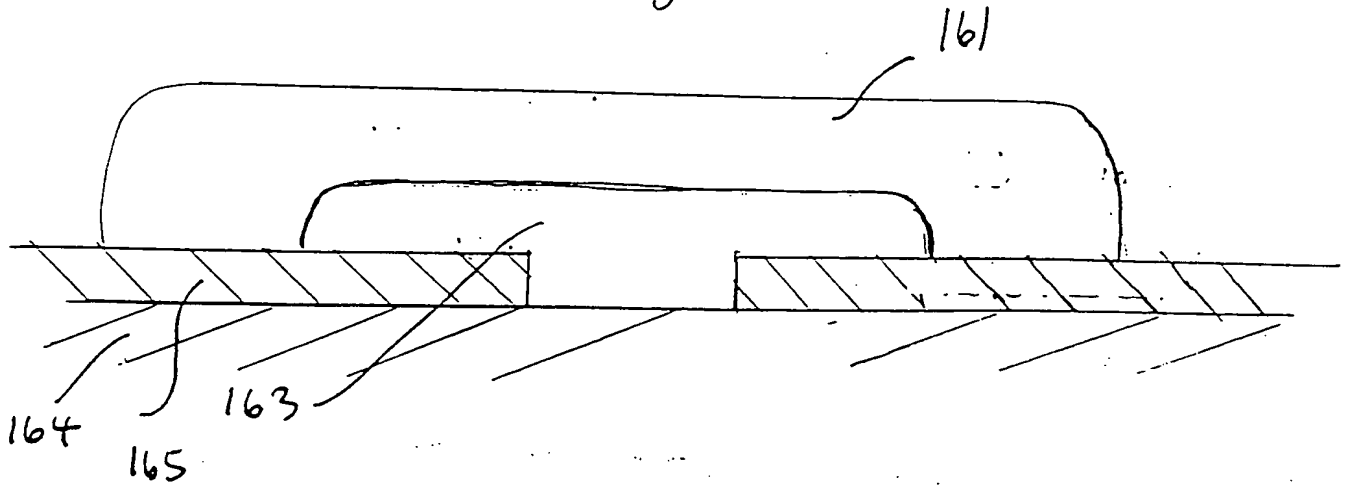
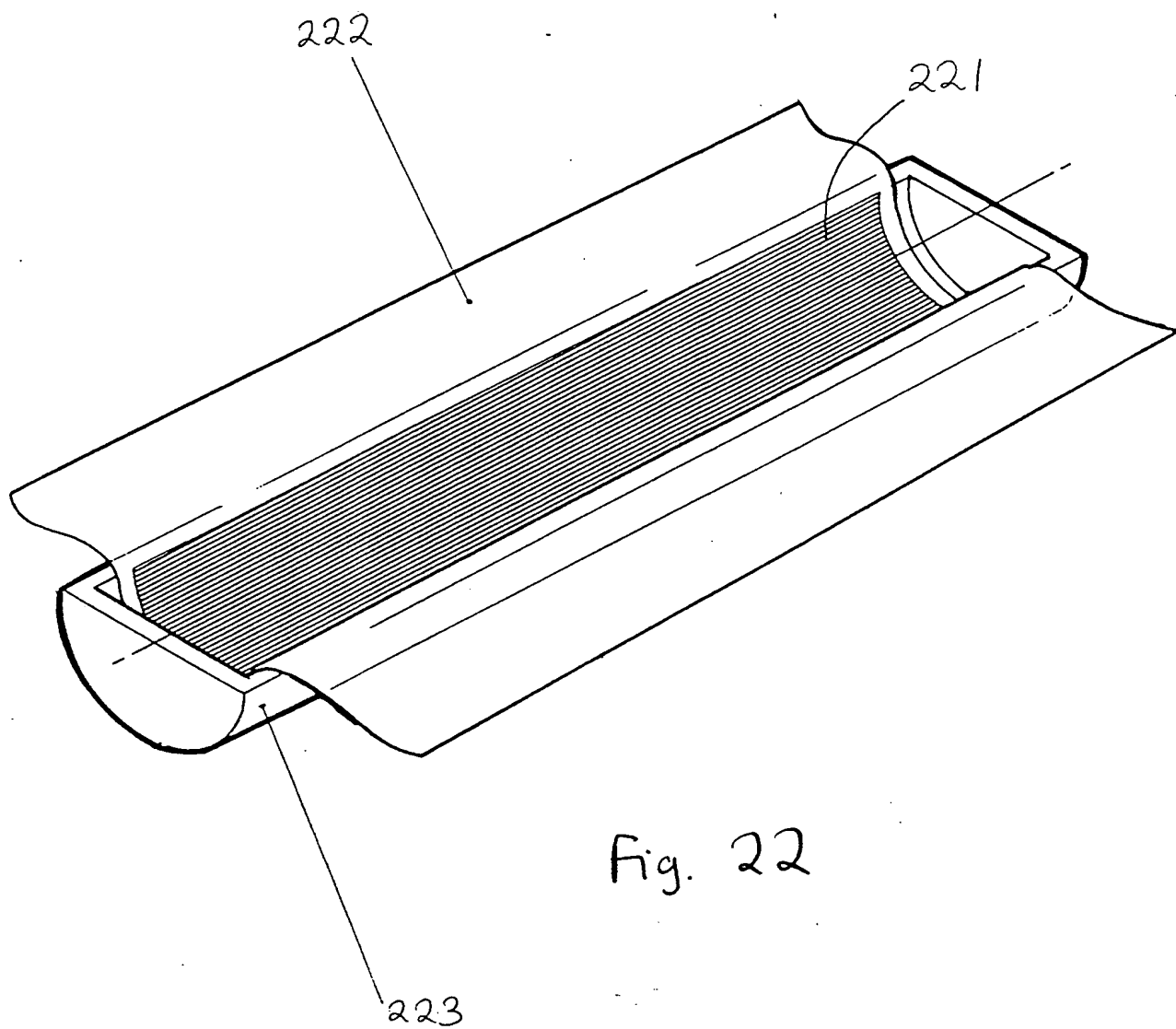


Fig. 21

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% Hoffman, Eitle & Partner
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Switchboard: 01633 814000
Fax: 01633 814444

Your Reference: P11909rl/rp
Application No: GB 9708848.8

27 June 1997

Dear Sirs

Patents Act 1977: Search Report under Section 17(5)

I enclose two copies of my search report and two copies of the citations.

In respect of the Y designations on the search report:-

- a) US 5527656 or EP 0493644 A1 is to be combined with any of GB 2230871 A, GB 1472462 or EP 0607680 A2, and
- b) US 5288377 is to be combined with EP 0607680 A2

Plurality of invention

I consider that your application relates to more than one invention as follows:

- i) The method of producing an electroformed article as set out in claims 1-11, 17 and in part 18 (NB figs 7-10,13,18) and the articles produced by such a method as claimed in claims 19-21;
- ii) The method of manufacturing a three-dimensional electroforming mask as claimed in claim 12 which is only **suitable** for use in invention a);
- iii) The method of manufacturing a three-dimensional electroforming mask as claimed in claims 13-16 and in part 18 (NB fig 16) which is different from the method of invention a) and again is only **suitable** for use in invention a); and
- iv) The method as claimed in part in claim 18 with reference to the embodiment illustrated in fig 22 (see also pages 25-26) where the surface is not flat.

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My search report relates to the first invention only. If you want any of the other inventions searched, you should file a separate Patents Form 9/77 for each invention.

Publication

I estimate that, provided you have met all formal requirements, preparations for publication of your application will be completed soon after **22 September 1998**. You will then receive a letter informing you of completion and telling you the publication number and date of publication.

Amendment/withdrawal

If you wish to file amended claims for inclusion with the published application, or to withdraw the application to prevent publication, you must do so before the preparations for publication are completed. **No reminder will be issued.** If you write to the Office less than 3 weeks before the above completion date, please mark your letter prominently: **"URGENT - PUBLICATION IMMINENT"**.

Yours faithfully

P. C. Beddoe

Peter Beddoe
Examiner

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Application No: GB 9708848.8 Examiner: Peter Beddoe
Claims searched: 1-11,17, in part 18, & 19-21 Date of search: 26 June 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7B (BBPA, BBRA, BCKK, BCPC, PCPM, BBPL, BCCE, BCCJ, BCCL, BCPD, BCPN, BCFX); G2X XB20X

Int Cl (Ed.6): C25D (1/00, 1/08, 1/10, 1/12, 1/14, 1/16, 1/18, 13/00, 13/02, 13/04, 13/06, 13/08, 13/10, 13/12, 13/14, 13/16); G03F (5/24, 7/00, 7/16); B26B 19/38

Other: Online: WPI, EDOC(QUESTEL)

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2230871 A (COATES) see ex 1 esp at p16 line 13 - p17 line 17	1
Y	GB 1472462 (HERSTAL) see esp claim 1, p2 lines 24-31 & p3 lines 30-33	1
Y	EP 0607680 A2 (WISCONSIN) see esp claim 1 & col19 lines 23-38	1
X	EP 0507043 A2 (SHIPLEY) see esp p5 lines 48-53 & p6 lines 8-43	1
Y	EP 0493644 A1 (SHIPLEY) see whole doc	1
X	EP 0407951 A2 (SHIPLEY) see esp ex 1 and steps 2-4	1
Y	US 5527656 (KANSAI) see esp exs	1
X	US 5512154 (MECO) see esp claim & exs	1
Y	US 5288377 (MACDERMID) see esp exs	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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